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Based on support from AROD, we have investigated redox and photochemical events in polypyrrole based polymeric films, and charge transfer processes in systems containing more than one redox site covalently attached to either soluble polymer or to solid supports. Binding and electrode position of metal particles into vinyl-bipyridyl based films were also achieved. Optical and thermal electron transfer in mixed-valence dimeric systems were studied in some detail.

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Based on support from AROD, we have investigated redox and photochemical events in polypyrrole based polymeric films, and charge transfer processes in systems containing more than one redox site covalently attached to either soluble polymer or to solid supports. Binding and electrodeposition of metal particles into vinyl-bipyridyl based films were also achieved. Optical and thermal electron transfer in mixed-valence dimeric systems were studied in some detail.

I. Chemistry in Polymeric Films

(i). Photocurrents in Thin Polymeric Films. Chromophore/Quencher Assemblies Based on Polypyrrole.⁶

Thin films of polymers consisting of mixtures of poly-N,N-bis(3-pyrrol-1-ylpropyl)-4,4'-bipyridinium dication (poly-(pyr)₂-PQ²⁺) and poly-tris-[4-(2-pyrrol-1-ylethyl)-4'-methyl-2,2'-bipyridine]ruthenium(II) dication, poly-(pyr)₃-[Ru]²⁺, have been prepared by co-oxidative electropolymerization of the corresponding pyrrole containing monomers. Significant photocurrents are observed when the films are photolyzed in the presence of the irreversible electron transfer donor, triethanolamine (TEOA). The initial step in the photocurrent mechanism is static, oxidative quenching of the metal to ligand charge transfer (MLCT) excited states of the ruthenium complex by poly-(pyr)₂-PQ²⁺. This gives poly-(pyr)₂-PQ⁺ and poly-(pyr)₃-[Ru]³⁺. The photoproduct -[Ru]³⁺ is subsequently reduced by TEOA. The photocurrent arises by electron transfer to the electrode at the electrode/film interface via the poly-(pyr)₂-PQ^{2+/-} couple.

A kinetic model has been derived which explains variations in the photocurrent with light intensity and [TEOA]. The magnitude of the photocurrent depends upon the composition and microstructural array of the chromophore-quencher assembly. Photocurrent efficiencies rise as the ratio of poly-(pyr)₂-PQ²⁺ to poly-(pyr)₃-[Ru]²⁺ increases in copolymeric films. High efficiencies require close contact and intermingling between the -[Ru]²⁺ and -PQ²⁺ sites. The conjugated poly-pyrrole backbone decreases the efficiency by competitive light absorption and by energy transfer quenching of the MLCT excited state. Under maximal conditions, per photon absorbed quantum efficiencies for photocurrent production of greater than 10% have been achieved.

(ii). Metal Ion Binding and Electrodeposition of Metal Particals in Films of poly-
Fe(vbpy)₂(CN)₂, poly-vbpy ¹³

Films of poly-[Fe(vbpy)₃](PF₆)₂ (vbpy is 4-methyl,4'-vinyl-bipyridine) have been cast on Pt⁰-, GC- (Glassy Carbon), and ITO-electrodes by the reductive electropolymerization of [Fe(vbpy)₃](PF₆)₂ in acetonitrile solution containing [n-Bu₄N]PF₆. The reaction between films of poly-[Fe(vbpy)₃](PF₆)₂ and [n-Bu₄N]CN in acetonitrile at room temperature resulted in the formation of films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy. The dicyano films react with PdCl₂(BN)₂ in acetonitrile at room temperature to give films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy•2PdCl₂. Spectroscopic as well as electrochemical data suggest that the PdCl₂ units are bound to the nitrogen atoms of the cyano groups in the dicyano films. Electrochemical reduction of films of poly-Fe(vbpy)₂(CN)₂, poly-vbpy•2PdCl₂ in acetonitrile resulted in the formation of films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy•Pd. The reduced palladium may exist as discrete Pd(0) complexes in the film or perhaps as small clusters. The reduced films are active toward the electrocatalytic reduction of CO₂. A Fischer-Tropsch type of product distribution was observed in the reduction of CO₂ by palladium particles dispersed on carbon paste electrodes in wet acetonitrile.

Thin films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy react with [Rh(COD)Cl]₂ in CH₃CN at room temperature to form films of poly-Fe(vbpy)₂(CN)₂,poly-Rh(vbpy)(COD)Cl. The electrochemical properties of the resulting films suggest that the [Rh(COD)Cl] unit is bound to the uncoordinated vbpy unit in the film. The electrochemical reduction of films of poly-Fe(vbpy)₂(CN)₂,poly-Rh(vbpy)(COD)Cl and the catalytic properties of Rh particles in the dicyano films are under investigation.

Films of the type poly-Fe(vbpy)₂(CN)₂,poly-vbpy • xMⁿ⁺ (M = Ag⁺, Cd⁺⁺, Ni⁺⁺) have been obtained from the reaction of the dicyano films in 0.1 M [n-Bu₄N]PF₆/CH₃CN solution with the particular metal ion at room temperature. The binding and electrochemical reduction of Ag⁺ have been studied in detail. Films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy • xAg⁺ undergo both oxidative or reductive loss the cyano groups to reform films of poly-[Fe(vbpy)₃](PF₆)₂. The electrochemical reduction of films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy • xAg⁺ resulted in the electrodeposition of small silver clusters in films of poly-[Fe(vbpy)₃](PF₆)₂. The location of the silver particles in films of poly-[Fe(vbpy)₃](PF₆)₂ is a function of both the time and the potential of the electrolysis. Single scan reduction of films of poly-Fe(vbpy)₂(CN)₂,poly-vbpy • xAg⁺ resulted in the dispersion of silver through out the films. The reduction of films of poly-

$\text{Fe}(\text{vbpy})_2(\text{CN})_2 \cdot \text{poly-vbpy} \cdot x\text{Ag}^+$ at -0.7 V resulted in the localization of silver particles near the electrode surface.

(iii) Electrocatalytic Reduction of Nitrite and NO by Iron(III) Protoporphyrin IX Dimethyl Ester Immobilized in an Polymeric Film ¹⁰

Thin polymeric films formed by anodic electropolymerization of Fe(III) protoporphyrin IX, dimethyl ester $[\text{Fe}(\text{PP})\text{Cl}]$, are effective catalysis for the electroreduction of HONO/NO_2^- or NO to N_2O , N_2 , NH_2OH , and NH_3 . The yield of N_2 is enhanced in the compact environment of the redox polymer relative to that for comparable monomeric metalloporphyrins in homogeneous solution.

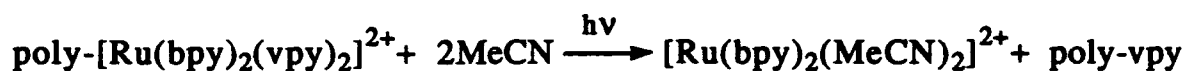
(iv). Oxidation Catalysis in Electropolymerized Films ¹²

Electrodes coated with thin polymeric films of $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}/\text{poly-cis}[\text{Ru}(\text{vbpy})_2(\text{H}_2\text{O})_2]^{2+}$ (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) or $\text{poly-cis}[\text{Ru}(\text{pyr-bpy})_2(\text{H}_2\text{O})_2]^{2+}$ (pyr-bpy is 4-(2-pyrrol-1-yl-ethyl)-4'-methyl-2,2'-bipyridine) were prepared and characterized by electrochemical and spectroscopic measurements. The results were compared with the solution chemistry of the analog monomers. The application of the pyr-bpy based films to the electrocatalytic oxidation of benzyl alcohol was studied by rotating disk voltammetry. An estimation of the rate constant for the mediation process and of the product of the equilibrium constant (for the formation of the association complex between the Ru complex and the substrate) and the partition coefficient (for the substrate) within the polymeric film was made. The mechanism of catalytic oxidation of benzyl alcohol in solution and in the polymeric film appears to be the same as demonstrated by a large isotope effect which supports hydride abstraction.

(v). Photochemical Imaging and Structure Building in a Thin Polymeric Film ⁸

In previous work it has been shown that some metal to ligand charge transfer photochemistry, including excited state electron transfer and the photochemically induced oxidation of metal-metal bonds, can be translated to thin polymeric films containing appropriate complexes. We have found that ligand loss photochemistry occurs in an electropolymerized film of $\text{poly}[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$ (vpy is 4-vinylpyridine) and related

derivatives. The utilization of this photochemistry in coupled electrochemical/photochemical cycles has allowed us to prepare a series of three-dimensionally resolved, film-based structures on conducting substrates. The net photochemistry involves extrusion of the metal complex unit by ligand loss.



The photochemistry can be carried out with spatial control to create patterns on a conductive substrate by using masking techniques. This leaves poly-[Ru(bpy)₂(vpy)₂]²⁺ in the masked areas and bare electrode in the photolyzed areas. Once formed, it is possible to fill the photochemically produced "holes" by formation of a second polymer at the bare electrode part of the pattern. This is achieved by a second electropolymerization step in which an imaged electrode is cycled reductively in a solution containing [Os(vbpy)₃]²⁺ to give poly-[Os(vbpy)₃]³⁺. By using a second photochemical cycle, it is possible to create a "negative" of the original pattern. Photolysis leads to loss of the remaining Ru complex while poly-[Os(vbpy)₂]²⁺ is photochemically stable.

II. Chemistry Involving Covalently Attached Species on Soluble Polymers and Monolayers on Solid Supports

(i). Synthesis and characterization of soluble polymers containing electron and energy transfer reagents ²

A series of monofunctional redox polymers containing a visible chromophore [tris-(bipyridyl) ruthenium(II) derivatives] or an organic energy transfer reagent (derivatized anthracene) were synthesized by reaction of poly(*m,p*-chloromethylstyrene-*co*-styrene) with alkoxide or carboxylate nucleophiles. Bifunctional polymeric materials incorporating anthracene and a reductive organic electron transfer quencher (phenothiazene) were prepared by analogous stepwise procedures. The degree of loading of the modified polystyrenes was controlled in a reproducible manner and have been verified by ¹NMR, UV-visible spectroscopy, and elemental analysis. Results from cyclic voltammetry confirm the electroactivity of the pendant functionalities and are consistent with a hydrophobic

environment surrounding the redox sites. Comparison of the steady-state emission spectra of the ruthenium(II) polymers with monomeric models indicates that the excited states properties of the metal complex are maintained upon polymeric attachment.

(ii). Molecular Level Electron Transfer and Excited State Assemblies on the Surface of Tin Oxide and Glass ⁹

A general procedure has been developed for the attachment of redox or photo-active groups to tin dioxide or glass surfaces based on the interaction between carboxylic acid and surface hydroxyl groups. The groups attached include derivatives of phenothiazine, methyl viologen, and $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy is 2,2'-bipyridine). The presence of the surface-attached groups has been verified by electrochemical and photochemical and photophysical measurements. From the electrochemical data surface coverages of molecular monolayers have been achieved reproducibly. Photophysical measurements, resonance Raman and infrared data have provided insight into the nature of the surface linkage. Formation constants for surface binding have been measured. Two techniques have been developed for preparing molecular assemblies in which more than one type of molecule attached to the same surfaces. Solution redox and excited state properties are largely preserved for the surface-attached molecules, but some special features do emerge.

(iii). Monolayer Assemblies on Glass and Metal-Oxide Substrates

Efforts to explore the redox behavior of molecular assemblies attached to conductive metal-oxide substrates have been expanded to include monolayer assemblies of dimeric complexes designed to exhibit spatially directed electron transfer. Investigations have shown that for the surface-attached complex $(4,4'-(\text{COOH})_2\text{bpy})_2(\text{Cl})\text{Ru-BPA-Os}(\text{Cl})(\text{bpy})_2$, (bpy = 2,2'-bipyridyl; BPA = bis-bipyridylethane) the limited electronic communication between the metal centers creates a scan rate regime in cyclic voltammetry where rectification effects begin to become apparent. Evidence for this behavior is that the integrated current for the $\text{Os}^{\text{III/II}}$ couple (0.5 V vs SSCE) is reduced with respect to the $\text{Ru}^{\text{III/II}}$ couple (1.3 V vs SSCE) as indicated by cyclic voltammetry. Results indicate that the $\text{Os}^{\text{III/II}}$ wave is composed of two components with one wave being scan rate dependent and one that is invariant. This behavior has been attributed to the different dispositions of the Os metal center with respect to the electrode. Unfortunately, with the synthetic

methodology utilized to obtain this complex (and a related series of complexes), the Ru center can be ester-linked to the electrode in such a way as to allow the Os center to be in a desirable position remote from the electrode or in an undesirable position adjacent to the electrode. These geometries would explain the scan rate dependent (due to hindered heterogeneous electron transfer from Os to the electrode) and independent components (due to facile communication of Os with the electrode) of the voltammetric waves respectively. Work is currently underway to synthesize improved molecular systems which should be capable of exhibiting this directional "rectifying" electron transfer behavior.

III. Intramolecular Processes

(i) Temperature and pressure effects on charge transfer absorption bands ¹

The frozen dipole approximation of dielectric continuum theory is shown to apply to the glass-to-fluid transition for charge transfer absorption bands.

(ii). pH-Induced Intramolecular Quenching. Ligand-Bridged Complexes Containing Osmium and Ruthenium ⁵

In the ligand-bridged complex $[(\text{tpy})(\text{bpy})\text{Os}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ (tpy is 2,2':6',2''-terpyridine; bpy is 2,2'-bipyridine; 4,4'-bpy is 4,4'-bipyridine) and its mixed-valence analogue, pH-induced photophysical effects are observed which are triggered by proton loss from the bound aqua ligand. In the $\text{Os}(\text{II})\text{-Ru}(\text{II})(\text{H}_2\text{O})$ complex, $\text{Ru}(\text{II}) \rightarrow \text{bpy}$ metal to ligand charge transfer (MLCT) excitation is followed by rapid, efficient energy transfer to the lower energy $\text{Os}(\text{III})(\text{tpy}^{\cdot-})$ MLCT state. If the pH is raised so that $[(\text{tpy})(\text{bpy})\text{Os}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{OH})(\text{bpy})_2]^{3+}$ is the dominant form, the $\text{Os}(\text{III})\text{tpy}^{\cdot-}$ -based emission is quenched by the $\text{Ru}(\text{II})(\text{OH})$ site. the mixed-valence complex $[(\text{tpy})(\text{bpy})\text{Os}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{bpy})_2]^{5+}$ can be converted from this nonemitting, $\text{Os}(\text{III})\text{-Ru}(\text{II})(\text{H}_2\text{O})$, form, to its emitting form, $[(\text{tpy})(\text{bpy})\text{Os}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{OH})(\text{bpy})_2]^{4+}$, by using pH changes to adjust the electronic distribution in the ground state.

(iii).Energy Relationships in Optical and Thermal Electron Transfer. Temperature Dependence of an Intervalence Transfer Absorption Band ¹¹

The temperature dependence of the optical absorption band corresponding to the electron transfer process, $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+} [(bpy)_2ClRu^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ (pz = pyrazine; bpy = 2,2'-bipyridine), has been studied in CH₃OD and in a nitrile solvent mixture. The temperature dependences of $E_{1/2}$ for the component $Ru^{III/II}$ couples in this complex were also studied by cyclic voltammetry. The temperature dependence of the absorption band, which was quite large, $(\partial E_{op}/\partial T) = -10 \text{ cm}^{-1}\text{K}^{-1}$ in CH₃OD, $m = 0.035$, was found to be the same, within experimental error, as the temperature dependence of the difference between $E_{1/2}$ values for the $Ru^{III/II}$ couples. This agreement provides experimental evidence that the absorption band energy includes the free energy change between the initial and final states and not just the change in enthalpy or internal energy. It is also consistent with the predictions of a model proposed by Marcus and Sutin for electron transfer reactions that is based on free energy surfaces. A temperature dependence in absorption or emission band energies is also predicted by a quantum mechanical model that is based on potential energy surfaces and harmonic oscillator wavefunctions. The temperature dependence appears once differences in frequencies and reorganizational energies between the initial and final states are included and arises from the free energy change of the reaction.

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AROD Related Manuscripts Submitted or in Preparation

9. Molecular Level Electron Transfer and Excited State Assemblies on the Surfaces of Tin Dioxide and Glass, J. Meyer, X. Chen, Jon Schoonover, T. J. Meyer, in preparation.
10. Electrocatalytic Reduction of Nitrite and NO by Iron(III) Protoporphyrin IX Dimethyl Ester Immobilized in an Electropolymerized Film J. N. Younathan, K. Wood, T. J. Meyer. *Inorg. Chem.* in press
11. Energy Relationships in Optical and Thermal Electron Transfer. Temperature Dependence of an Intervalence Transfer Band. J. T. Hupp, G. A. Neyhart, T. J. Meyer, E. M. Kober. *J. Phys. Chem.* in press
12. Oxidation Catalysis in Electropolymerized Films. A. R. Guadalupe, X. Chen, B. P. Sullivan, T. J. Meyer. Submitted.
13. Preparation, Solvatochromic, and Binding Properties of {poly-[Fe(vbpy)₂(CN)₂], poly(vbpy)}. M. Bakir, B. P. Sullivan, T. J. Meyer in preparation
14. Solvent Induced Electron Transfer and Delocalization in Mixed-Valence Complexes. Electrochemistry. G.A. Neyhart, J. T. Hupp, J.C. Curtis, T.J. Meyer in preparation

15. Solvent Induced Electron Transfer and Delocalization in Mixed-Valence Complexes. Spectroscopy. G.A. Neyhart, J. T. Hupp, J.C. Curtis, T.J. Meyer in preparation

Presentations

1. Ligand Exchange Reactions in Polymeric Thin Films, X. Chen, A. R. Guadalupe and T. J. Meyer, *Pittsburgh Conference*, March 6-10, 1989, Atlanta, GA.
2. Formation of an oxo-bridged dimer in Thin Polymeric Films, X. Chen and T. J. Meyer, *ACS Regional Conference*, Chapel Hill, April 15, 1989

Pending Patent Applications

1. Photochemical Imaging and Structure Building in a Thin Polymeric Film. T. J. Meyer, T. O'Toole, S. Gould
2. Oxidation Catalysis in Electropolymerized Films. T. J. Meyer, A. Guadalupe, X. Chen, B. P. Sullivan

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